Appendix I. Chemical Analytical Method
For Group 1 Pesticides using GC
UC Davis Trace Analytical Laboratory

Protocol for Analysis of Lompoc Air Samples

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I. Proposed Chemicals for Analysis

Table 1 Contains the proposed list of compounds whose physicochemical properties may be compatible with a single sample multiresidue air sampling/analysis scheme using XAD-4 resin as a trapping medium. The compounds chosen in this table have the air sampling criteria of an airflow rate of 15 liters per minute (lpm) for a 24-hour sampling period, under normal weather conditions of the Lompoc region. Due to limited laboratory resources, the maximum number of compounds that could be analyzed this year will be confined to this list. The final list of compounds to be analyzed during Phase II will be determined after the method development phase is completed. The final list will be at least 25 compounds, and determined by TAL and DPR personnel.

Table 1: List of Candidate Compounds for a Multiresidue Air Sampling Scheme.

Compound	Trapping Experiments Completed	Storage Stability	Compatibility with single sample multiresidue analysis using XAD-4
Chlorpyrifos	X	X	X
Diazinon	X	X	X
Diazinon oxon			X
Malathion			X
Chlorpyrifos oxon			X
Fonofos	X	X	X
Fonofos oxon			X
Malathion oxon			X
Chlorthal-dimethyl			X
PCNB			X
Trifluralin			X
Dimethoate	X	X	X
Mefenoxam			X
Chlorothalonil	X	X	X
Dimethoate oxon			X
Anilazine			
Ethalfluralin			
Dicloran			
Dicofol			
Metolachlor			
Iprodione			
Simazine			
Cycloate			
Permethrin	X	X	X
Naled	X	X	X
Propyzamide			
Thiodicarb			

Vinclozolin			
Thiophanate-methyl			
EPTC			
Sulfur			

II. Proposed Analytical Method

The analytical method that will be used consist of the following:

Sample Extraction

Remove Teflon cap and screen from resin cartridge and pour resin into an appropriate wide mouth jar. Carefully rinse cartridge with 75 mL of ethyl acetate and add the solvent to the jar. Cap the jar with a Teflon lined lid.

Prepare three laboratory concurrent resin fortification samples by adding 30 mL of clean XAD-4 resin to an appropriate jar and fortifying the resin with a standard mixture of a known concentration and an appropriate syringe. Fortifications will be between 1 - 5 times the EQL. Add 75 mL of ethyl acetate and cap the jar.

Swirl for one hour, on a rotary platform shaker, at a moderate speed.

Sample Work up

Quantitatively transfer a 37.5 mL aliquot to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator.

Add 2.0 mL of ethyl acetate to the flask, cap and swirl.

Transfer an aliquot from the flask to a GC vial and inject on the GC/FPD and the GC/MSD analytical systems.

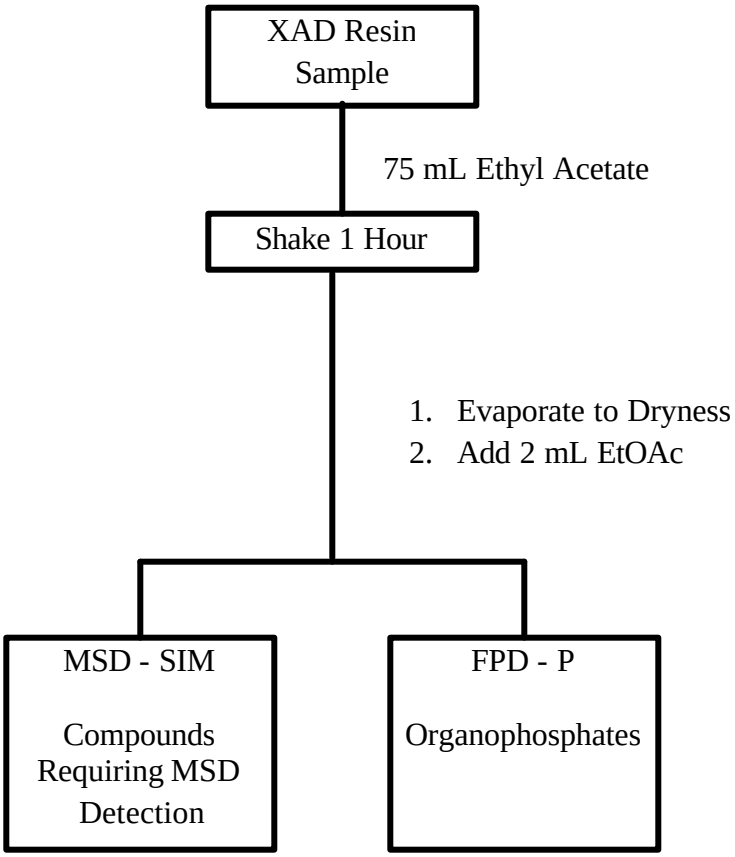
Inject 3 µL of sample for GC/FPD and 2 µL of sample for GC/MSD, along with the appropriate standard concentrations for each of the compounds listed in Table 1into the gas chromatographs. If the peak height/area for the compound of interest is larger than the highest standard, dilute the sample with ethyl acetate and re-inject.

Calculate the mass of the compound in µg, based on the linear regression curve from TurboChrom® (FPD) or Microsoft® Excel (MSD) and the appropriate dilution factors.

Concentration (µg/mL) x Dilution Factor (mL)/Sample = µg/sample.

A schematic of the sample analysis is given in Figure 1.

Figure 1. Method Schematic of Analysis for Lompoc Phase I Air Samples



Quality Assurance

For each set of samples analyzed, at least three laboratory concurrent fortified samples will be run to validate the set. The concurrent fortified samples will consist of control XAD-4 resin, resin that has been cleaned but not exposed to any chemicals, fortified in triplicate at one to five times the EQL. A control resin sample will also be analyzed with every set of air samples.

Selected samples, as mutually agreed to by TAL and the Department of Pesticide Regulation (DPR), will be confirmed with the Mass Selective Detector operated in selective ion monitoring mode (SIM). Confirmation of Table 1 compounds, in selected air samples, will include retention time and visual inspection of a set number of ions for a given compound. Further confirmation may include full spectrum scans and spectral library searches and/or comparison of ion ratios with standards and fortified resin samples. Spectral library searches will depend on the degree of background in the sample and the concentration of the compound of interest. Confirmation will be qualitative not quantitative.

The quality assurance unit (QAU) of the TAL will provide one set of blind samples for each week of sampling. The blind set will consist of three samples spiked at a concentration known only to TAL's QAU personnel, and a control resin sample. The concentration of these fortified samples will be 2 to 5 times the EQL, and may be increased depending on monitoring results. Each set will be fortified and analyzed during the period of time that air sampling is conducted in the Lompoc region. TAL personnel will report the amount in each sample as the total mass of that sample.

TAL's QAU will do at least one critical phase inspection of the ongoing analysis during the analytical phase of the project.

III. Estimation Of Detection Limits And Limit Of Quantitation.

The estimated quantitation limit (EQL) can not be determined until the method detection limit for each compound is determined during the method development phase of the project. However, using data generated for the ten compounds in Phase 1, a predicted estimated quantitation limit would be in the range of approximately 3 to 6 ng/m^3 for organophosphates and 6 to 20 ng/m^3 for compounds that require the use of a MSD for detection. This is based on a air flow rate of 15 lpm and a sampling period of 24 hours. The EQL and the MDL for non-organophosphates will vary more because the detector sensitivity is dependent on the ionization potential of each compound. Aromatic chlorinated compounds have a higher ionization potential than an aliphatic compound. The EQL and MDL for each of the Phase 1 compounds are given in the method development section, Table 3.

IV. Method Development

Preliminary work

While trapping efficiency, storage stability and method detection limit determination has been done for approximately a third of the compounds in Table 1, they must be done for the remaining compounds listed. Also, instrument parameters, including column liquid phase, oven temperatures, flow rates and quantitation ions, must be optimized to insure separation from potential interferences.

The preliminary laboratory effort will include the following: 1) Procurement and preparation of standards; 2) The preparation of air sampling medium; 3) optimization of analytical systems employed for the analysis of the compounds listed in Table 1.; 4) Initiation of a freezer storage stability study; 5) The determination of the method detection limit (MDL) according to USEPA guidelines (40CFR 136); 6) determine the trapping efficiencies for those compounds not cited in the literature or not been determined in Phase 1 of the Lompoc study.

1. Preparation of Standards

   Prepare standards for preliminary work using standards from the existing laboratory repository (both GLP and non-GLP). Initiate procurement of certified standards for GLP analysis of air samples from the Lompoc air project. Stock solutions of each compound, in the appropriate solvent will be prepared. Fortification standard mixtures, dilutions of compatible compounds will also be prepared.

2. Preparation of XAD - 4 Resin Air Sampling Medium

   Bulk commercial grade XAD-4 resin is not sufficiently clean enough for multiresidue air sampling. The laboratory purification procedure of commercial grade XAD-4 resin used for air sampling is outlined in Appendix A. An adequate supply of resin will be precleaned from a single batch and screened for potential interferences prior to the start of the sampling phase of the project.

3. Optimization of analytical systems

   The intended analytical instruments for multiresidue analysis of the compounds listed in Table 1, will consist of gas chromatographs equipped with either flame photometric detectors using phosphorus mode, or Mass Selective Detectors (MSD), operated in selective ion monitoring mode (SIM). Due to the complexity of the analysis, a Hewlett Packard (HP) 5890 Series II gas chromatographs equipped with flame photometric detector (FPD) and phosphorus filter (526 nm), will be employed for the analysis of organophosphates and their oxons. The FPD has a high degree of sensitivity and selectivity when operated in the phosphorus mode. Furthermore, the FPD is very stable for long periods of time, which lends itself well for the analysis of large analytical sets (runs).

   For the analysis of compounds other than organophosphates, two gas chromatographic mass spectrometer systems (GC/MS) will be employed. Both GC/MS systems will be a Hewlett Packard 6890 gas chromatograph with a 5972 mass selective detector (MSD) and a 6890 gas chromatograph with a 5973 MSD. These systems will be used for analysis and selective confirmation of Table 1 compounds in air sample extracts.

   All systems will be optimized with columns of varying liquid phases for optimal separation of the compounds of interest from potential interferences and other compounds.

4. Storage Stability

   A storage stability study will be initiated approximately six weeks prior to the start of air sampling and terminated four weeks there after. The study will be initiated by fortifying 20 replicates of resin samples, 30 mL each, with all compounds that have no storage stability history. Eight of the replicates will be extracted initially and analyzed. The remaining storage samples will be stored at approximately -20 °C for four weeks. At that time, four replicates will be analyzed while the remainder will stay in storage for the duration of the study and only analyzed if needed.

5. Determination of method detection limit

The method detection limit (MDL) will be determined for each of the compounds where there is no previously reported MDL. The MDL will be determined either by fortifying the resin directly and analyzing without pulling air through the resin. The study will include eight replicates fortified at 0.20 µg each. The results of a MDL experiment for Phase 1 compounds are listed in Table 2 while the EQL in ng/m3 is given in Table 3. The MDL for alachlor was calculated as follows:

MDL = t x s, where t is students' t values at the 99 percent confidence level and s is the standard deviation of the eight replicate samples analyzed.

MDL = 2.998 x 4.70 = 14.1 pg/µL

And the estimated quantitation limit (EQL) is five times the MDL, or

EQL = 5 x MDL = 70.5 pg/µL

Table 2. Pesticide Method Detection Limits and Estimated Quantitation Limits.

Sample Number	Alachlor (pg/ul)	Chlorothalonil (pg/ul)	Chlorpyrifos (pg/ul)	Diazinon (pg/ul)	Dimethoate (pg/ul)	Disulfoton (pg/ul)	Fenamiphos (pg/ul)	Fonofos (pg/ul)	Oxydemeton (pg/ul)	Permethrin (pg/ul)
MDL-1a	33.4	36.0	23.6	19.1	21.4	26.4	32.4	16.0	47.8	29.4
MDL-2a	41.7	38.9	23.7	18.1	19.0	24.1	30.2	15.0	47.1	37.1
MDL-3a	36.0	31.2	23.8	19.0	20.9	26.2	29.9	15.1	47.2	32.4
MDL-4a	35.8	33.6	27.9	23.4	24.3	29.7	34.0	20.1	51.4	34.9
MDL-5a	28.5	34.4	22.8	17.6	20.0	26.0	31.8	15.1	46.7	27.6
MDL-6a	29.6	34.9	24.4	19.3	21.5	27.0	32.3	16.1	47.3	30.3
MDL-7a	29.9	32.9	25.2	20.7	23.2	28.0	33.4	16.9	50.5	33.3
MDL-8a	28.4	29.1	23.3	18.8	20.6	26.8	31.3	16.4	48.6	31.1
Average=	32.9	33.9	24.3	19.5	21.4	26.8	31.9	16.3	48.3	32.0
Stdev=	4.70	2.99	1.62	1.81	1.72	1.63	1.44	1.68	1.74	3.07
MDL=	14.1	8.95	4.87	5.44	5.16	4.89	4.32	5.03	5.21	9.21
EOL=	70.5	44.7	24.3	27.2	25.8	24.5	21.6	25.1	26.1	46.1

Based on the 4.0 mL extraction volume and assuming a sample volume of 28.8 m^3 (30 lpm for 24 hours) the ambient concentration of the pesticide at the EQL is:

$$\frac{70.5\frac{ng}{mL}\times 4.0\,mL}{28.8\,m^3} = 9.79\frac{ng}{m^3}$$

Table 3. Ambient Concentration of Pesticides at the Estimated Quantitation Limit for Phase 1 Compounds.

Alachlor (ng/m^3)	Chlorothalonil (ng/m^3)	Chlorpyrifos (ng/m^3)	Diazinon (ng/m^3)	Dimethoate (ng/m^3)	Disulfoton (ng/m^3)	Fenamiphos (ng/m^3)	Fonofos (ng/m^3)	Oxydemeton (ng/m^3)	Permethrin (ng/m^3)
9.79	6.21	3.38	3.78	3.58	3.40	3.00	3.49	3.62	6.40

It is assumed that the candidate compounds listed in Table 1, will have roughly the same MDL and EQL range as for those compounds previously determined.

6. Trapping Efficiencies

TAL will either determine air-trapping efficiencies or provide suitable documentation of such assessing trapping efficiency using the proposed analytical procedures. Trapping efficiencies will be provided at one spiking level.

Compounds will be fortified at 50 µg on glass wool directly above two sampling cups in tandem. The first cup will serve as the primary trap while the second cup is the backup cup to check for breakthrough. There will be four replicates for each compound. The experiment will be done with sampler flow rates at approximately 30 liters per minute (lpm), twice the intended field flow rate and run for at least 24 hours.

V. Sample and Reporting Turnaround Time

Preliminary results will be reported within six weeks of receipt of samples.

VI. Laboratory Personnel

The following list is of laboratory personnel that will tentatively work on this project. The percentage of time spent on the project will be dependent on other prior assigned duties/tasks, and on the sampling duration of this project.

Chuck Mourer	TAL Laboratory Manager, Project Manager, Principal Analyst.
Matt Hengel	Data Analyst, Weekly Contact Person, Assistant Project Manager
Greg Hall	Data Analyst, Laboratory SOP Supervisor
To Be Named	Analyst, Wet Chemistry, Data Analysis
Bronson Hung	Analytical Support, Wet Chemistry, Data Analysis
Michael McChesney	Analyst, Wet chemistry
James Stokes	Standard Control Officer
Jim McFarland	GLP Officer
Riza Reyes	Research Technician

VII. Other Considerations

UC Davis reserves the right to publish any method developed at UC Davis or by University personnel, and pertinent data that supports the validation of said method.

This is to be a best-effort undertaking and unforeseen circumstances which preclude obtaining the analytical results required by DPR, after a best-effort attempt, will not negate the contract. If

additional analysis for metabolites and/or breakdown products is required, then additional funding will be necessary.

VIII. Management Plan

1) Professor Taka Shibamoto, Mr. Charles Mourer and Mr. Michael McChesney will be responsible for the development of sampling and analytical techniques that can be applied to the selected pesticides. DPR and Air Resources Board personnel will be responsible for locating treatment sites, for collecting field samples using the techniques to be developed by Mourer and McChesney, and for transporting the samples safely to the laboratory. Once received, Mr. Mourer will be responsible for resin preparation, sample handling, work up, and analysis, under Dr. Shibamoto's supervision.

2) Data summaries for the initial trapping efficiencies/storage stability and MDL experiments will be provided prior to the start of the ambient air sampling phase. Data summaries will be presented after all samples are analyzed.

3) Progress reviews may be conducted 1- 2 times during the course of the project. TAG and UCD personnel will meet for these reviews and the meetings will alternate between the Sacramento and UCD facilities.

IX. Sampling Plan and Number of Samples

DPR will monitor three to four sites in Lompoc, with possibly one site duplicated for quality control. Each site will be sampled three to four times each week for eight to ten weeks.

TAL will include eight quality control samples for each week of sampling. These samples will include four field quality control samples: one control (blank), two blind fortification samples (field spikes), and a trip spike. The samples will include four laboratory quality control samples: three fortified resin samples and a control resin sample. Validation samples will be fortified between two to five times the EQL.

TAL will analyze 20 – 24 samples each week (including quality control) for eight to ten weeks. TAL will analyze a total of 192 – 230 samples.

TAL may request additional analyses for oxydemeton-methyl, or identification of unknown chemicals. The number samples and specific analyses will be negotiated between TAL and DPR prior to the submission of samples.

X. Proposed Time line

The following is a proposed Time line to coordinate activities

	Preliminary Work
+ Week Eight	All supplies ordered (solvents, glassware, GC columns). GLP standards are ordered. Cleaning of XAD-4 resin is initiated.
+Week Seven	Standard solutions are prepared. Instrumentation optimization is initiated. Laboratory method recovery, trapping efficiencies, and a four-week freezer storage stability

	study are initiated. Air sampling medium preparation continues. Air trapping experiments initiated.
+Week Two-Six	Multiresidue LOQ is determined. Laboratory method recovery, trapping efficiencies studies continue.
+ Week Two	Analysis is completed on freezer storage stability experiments. Multiresidue method undergoes final optimization. Air sampling medium preparation is terminated. TAL submits a progress report to Lompoc Technical Advisory Group (TAG). TAG/ARB finalizes the location for the ambient site samples
+ Week One	Air sampling medium is deliver (picked up) by assigned sampling personnel.

Ambient Air Sampling

Week Zero	Ambient air sampling by sampling personnel commences. At the end of the week, sampling personnel delivers samples to TAL. TAL personnel initiate analysis of ambient site samplin g.
- Week One	Second week of ambient site sampling is conducted by sampling personnel; TAL personnel analyze samples.
- Week Two	Third week of ambient site sampling is conducted by sampling personnel; TAL personnel analyze samples.
- Week Three	Fourth week of ambient site sampling is conducted by sampling personnel; TAL personnel analyze samples.
- Week Four	Fifth week of ambient site sampling is conducted by sampling personnel; TAL personnel analyze samples
- Week Five	Sixth week of ambient site sampling is conducted by sampling personnel; TAL personnel analyze samples.
- Week 6 –10	Same procedures as for Week 0 – 5.

Post Air Sampling

- Week 11	Laboratory analytical/confirmation work finalized.
- Week 12 - 13	Analytical Data is review and summarized.
-Week 14	Final data package is submitted to the Study Director.

XI. Budget

Method development (Section IV) - method optimization - method detection limit determination - storage stability - trapping efficiency	$25,000
Routine analysis for 25 – 30 pesticides (Section IX) $730/sample X (192 - 230 samples)	167,900
Special analysis (Section IX) - identification of unknown chemicals - analysis for oxydemeton-methyl	7,100
Administrative overhead (10%)	20,000
TOTAL	$220,000

Appendix A. Preparation of XAD-4® Resin

1. Add 10-14 liters of XAD-4 resin to a 61 x 29 cm cylindrical Pyrex container (~ 40 L), or equivalent.

2. Wet the resin with one gallon of methanol (Resi-grade or equivalent. [Caution: The resin will expand in the presence of organic solvents.]).

3. Remove fines by overfilling the container with deionized water with the hose placed at the bottom of the container and stirred vigorously.

4. Add two liters of 0.25 N hydrochloric acid and stir for 30 minutes.

5. Add water to the top of the vessel and decant off the fines and excess water.

6. re-filled with DI water and stir.

7. Repeat steps #5 and 6 were until the water above the resin was clear and the pH is that of the deionized water.

8. Transfer with methanol to gallon bottles.

9. Transfer resin to a large Soxhlet extractor and extract resin with methanol for 24 hours.

10. Add fresh methanol and extract for another 24 hours.

11. Extract resin with ethyl acetate for 24 hours. Add fresh ethyl acetate and extract for an additional 24 hours.

12. Dry the resin in a vacuum oven (25 in. Hg) for 3-4 days at 65°C or until all traces of ethyl acetate is gone from the resin.

13. Store resin in clean dry jars with Teflon® lined lids. Store at room temperature until time of use.

From: Matt Hengel <mjhengel@ucdavis.edu>
To: <pwofford@cdpr.ca.gov>
Date: 11/2/00 3:11PM
Subject: Lompoc

Ok here's our explaination of the some of the higher recoveries for the concurrent fortifications. In the process of conducting a multi-residue analysis, various conditions are optimized for the majority of the compounds. In the case of the Lompoc samples, the compounds analyzed on
the GC-MSD are particularly susceptible to enhancement from the resin matrix. In order to combat this problem standards were prepared in the presence of matrix (extracted resin material) to minimize the enhancement of recoveries. Alternatively, because so many standards are needed to insure linearity, we chose to reduce the matrix load in the standards to help extend the life of the analytical column. The amount of matrix was chosen to minimize the amount of resin material on column, while providing
enough matrix to reduce the enhancement of recoveries on the majority of the compounds. Unfortunately some compounds, ethalfluralin in particular,
are more sensitive to enhancement. As a result many of the compounds had
satisfactory recoveries, while other tended to have consistently higher recoveries. The aforementioned ethalfluralin, consistently had recoveries above the 120% point, except for week 6. In addition, during the course of
the ten weeks of analysis, other compounds would occasionally creep above
120% recovery. Again these compounds fall prey to enhancement (especially
at the lowest level of validation, where small gains in sensitivity can equate to larger recoveries). All the plus side of these analyses, the standard deviation for the 3 replicate concurrent recoveries where generally below 5%. Which would suggest that although the recoveries are
high, the method consistency is present. Also, the fortification standard was checked against the calibration standards for accuracy.

Too bad the world isn't a perfect place, such that we could do all of our analyses on a GC-FPD with a mega-bore column (which doesn't have the enhancement issues, as seen in the FPD data for the organo-phosphate compounds). Other than the high recoveries from ethalfluralin, we feel comfortable with other recoveries.

Attached is the procedure we used for the particulate filter samples.

Particulate Filter Procedure for PCNB, Vinclozolin, Dacthal, Dicofol, and Permethrin *via* GC-MSD

A. Sample Extraction

1. Remove Teflon cap and screen from resin cartridge and remove the glass fiber filter (GFF). Cut the filter into quarters and place into a 125 mL Erlenmeyer flask with 75mL of ethyl acetate. Homogenize the sample using an Ultra-Turrax T-25 for 2 minutes (13,500 rpm).
2. Prepare one laboratory control sample by with 75 mL ethyl acetate. Homogenize the sample using an Ultra-Turrax T-25 for 2 minutes (13,500 rpm).
3. Prepare three laboratory concurrent filter fortification samples by using a clean GFF filter, cut into quarters, and place in a 125 mL Erlenmeyer flask and fortifying the filter with a standard mixture of a known concentration using an appropriate syringe. Fortifications will be between 1 -5 times the estimated quantitaion limit (EQL). Add 75 mL of ethyl acetate and homogenize the sample using an Ultra-Turrax T-25 for 2 minutes (13,500 rpm).
4. Following homogenization, filter the sample extract using a Buchner funnel fitted with a Whatman GFF filter backed by a Whatman #1 filter using mild vacuum.

B. Sample Work up

1. Quantitatively transfer 37.5 mL of the filtered extract to a 100 mL round bottom flask and evaporate the solvent to dryness using a rotary evaporator.
2. Add 2.0 mL of ethyl acetate to the flask, cap and swirl.
3. Transfer an aliquot from the flask to a GC vial and inject on the GC/MSD analytical system.